Iraqi Journal of Chemical and Petroleum Engineering
Vol.16 No.1 (March 2015) 1- 12
ISSN: 1997-4884

Iraqi Journal of Chemical and Petroleum Engineering

University of Baghdad
College of Engineering

Performance of Corrosion Inhibitors Blend for Simulated Industrial Cooling Waters under Dynamic Conditions

Qasim J.M.Slaiman and Abeer A. Al-Khasab
Department of Chemical Engineering, College of Engineering, Al-Nahrain University, Iraq

Abstract

The inhibitive action of a blend of sodium nitrite/sodium hexametaphosphate (SN+SHMP) on corrosion of carbon steel in simulated cooling water systems (CWS) has been investigated by weight loss and electrochemical polarization technique. The effect of temperature, velocity, and salts concentrations on corrosion of carbon steel were studied in the absence and presence of mixed inhibiting blend. Also the effect of inhibitors blend concentrations (SN+SHMP), temperatures, and rotational velocity, i.e., Reynolds number (Re) on corrosion rate of carbon steel were investigated using Second-order Rotatable Design (Box-Wilson Design) in performing weight loss and corrosion potential approach. Electrochemical polarization measurements were used to study the behavior of carbon steel in different salts concentrations of (CWS) with pH = 7.5 in absence and presence of the inhibiting blend. The results show that the regression model (Box-Wilson Design) that has been developed using experimental data was used to verify that the interaction term of temperature with inhibitors blend and the square term of inhibitors blend are significant for corrosion rate in 0.05 N NaCl solution while the main variables are not pronounced. Also, it is found that the corrosion rate of carbon steel is increased with increasing temperature, rotational velocity, and NaCl salts concentration in uninhibited and inhibited solutions. Inhibition performance of $NaNO_2$+ $Na(PO_3)_6$ was found to increase with its concentration up to 800 ppm inhibitors blend, and the corrosion potential is shifted to more positive direction with increasing rotational velocity, and inhibitor blend concentration.

Key Words: Corrosion inhibitors, Cooling water systems, Sodium hexametaphosphate, Rotatable design (Box-Wilson Design).

Introduction

Understanding the effect of environmental factors is necessary in determining the rate of a metal corrosion. Each metal species will exhibit its own rate of corrosion. Environmental factors such as oxygen concentration, pH, chloride ion concentration and temperature are also known to influence the rate of corrosion [1]. Therefore, there is a need to protect these metals against corrosion. The best option available for the protection of metals against corrosion has been found to be using of inhibitors [2]. Cooling water systems are integral part of most industries and their performance is seriously affected by corrosion of materials and scale deposits. Use of inhibitors in controlling corrosion/scales in cooling water systems is an established technology. A number of inorganic/organic inhibitors have been used in the last sixty years [3]. Corrosion inhibitors retard the destruction of metals by chemical or electrochemical reactions with their environment. Most of the inhibitors used in cooling waters, are either alone or in combination with one or more corrosion inhibitors [4]. Most of inorganic inhibitors are toxic e.g., chromate, mercuride nitrite, arsenate etc. [5]. As a result, the current trend for inhibitor usage towards more environmentally friendly ‘green’ chemicals [6].

The aim of this work is to study the performance of corrosion inhibitors blend action of sodium nitrite / sodium hexametaphosphate on carbon steel rotating cylinder in different salt concentrations of cooling water systems at different temperatures (30, 45,& 60 ◦C) under dynamic conditions of different velocities (200,600, & 1000 rpm).

Experimental Method

Materials

Cylindrical carbon steel specimen was prepared to fit the specimen holder with a surface area of 19.6350 cm^2 having dimensions of 2.5 cm long (l), 1.9 cm inside diameter (d_i), and 2.5 cm outside diameter (d_o) that were measured using electronic digital caliper. Its composition is given in table (1):

Table (1), the chemical composition of carbon steel cylinder (Wt. %).

	Mn	V	Cr	Mo	Fe
0.06	0.93	0.05	3.51	0.35	Balance

Solutions

Four different tested solutions (un inhibited solutions) were prepared by dissolving four different concentrations of NaCl salt with 0.00736 N Na_2SO_4 in one litter of distilled water at pH of 7.5:

a. 0.005 N NaCl + 0.00736 N $Na_2SO_4^-$
b. 0.01 N NaCl + 0.00736 N $Na_2SO_4^-$
c. 0.03 N NaCl + 0.00736 N $Na_2SO_4^-$
d. 0.05 N NaCl + 0.00736 N $Na_2SO_4^-$

Inhibitors solutions were prepared by dissolving appropriate amounts of inhibitors as a blend of SN and SHMP in each tested solutions based on total ppm made of the two inhibitors as shown below:

e. 0.005 N NaCl + 0.00736 N $Na_2SO_4^-$ + 600 ppm (500 SN+100 SHMP).
f. The same tested solution **b** with two different concentrations of each inhibitor [600 ppm (SN+ SHMP)].

g. The same tested solution **c** with two different concentrations of each inhibitor [600 ppm (SN+ SHMP)].
h. The same tested solution **d** with different amounts of inhibitors blend according to Box-Wilson method [7].

The pH of the solution was adjusted using dilute solutions of NaOH or HCl.

Weight Loss Method

The metal specimens were abraded with glass emery paper of grades, 120, 180, 220, 400 and 2000 respectively, washing continuously with running tap water followed by distilled water, dried with Kleenex tissue, rinsed with acetone, followed by ethanol, dried with Kleenex tissue and left in desiccator for 20 hours, and then weighed accurately before using or introduced in the tested solutions. After test the specimens were visually observed, then washed with running tap water, cleaned with brush to remove the weakly adherent corrosion scale, washed with distilled water, swabbed with a piece of cotton soaked with inhibited hydrochloric acid to remove all adherent corrosion products, washed with running tap water, and then repeat the cleaning as in the beginning then left for 20 hour to dry in a desiccator over silica gel, and accurately weighed to the forth decimal of gram.

Polarization Technique

The electrochemical cell was composed of graphite counter electrode, prepared carbon steel specimen as working electrode and saturated calomel electrode (SCE) as a reference electrode. Corrosion potential ($E_{corr.}$) and polarized potential were measured against SCE. Corrosion cell parts (see Fig. 1) were then connected to ammeter and voltmeter. Cathodic polarization was performed until reaching the corrosion potential, then continuing with anodic polarization. The potential was changed (30-50 mV) for each step and after one minute period steady state current was recorded for each potential step. Also, it is to be stated that the experimental runs were repeated twice to four times to ensure accuracy and repeatability.

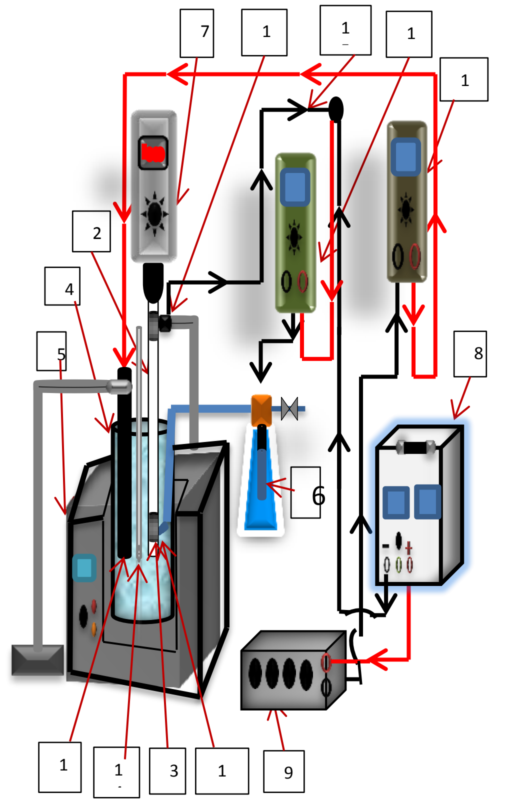

Fig.1, Corrosion-cell parts 1. Graphite electrode (anode), 2.Rotating shaft (holder), 3.Working electrode (specimen), 4.Beaker, 5.water bath, 6.Reference Saturated Calomel Electrode (SCE), 7.Stirrer, 8.Power supply, 9.Resistance box, 10.Voltmeter, 11. Ameter, 12. Luggin capillary tip, 13.Brush, 14.Thermometer, 15.Electrical wires

Results and discussion

1. Weight Loss Method

a. Uninhibited solutions

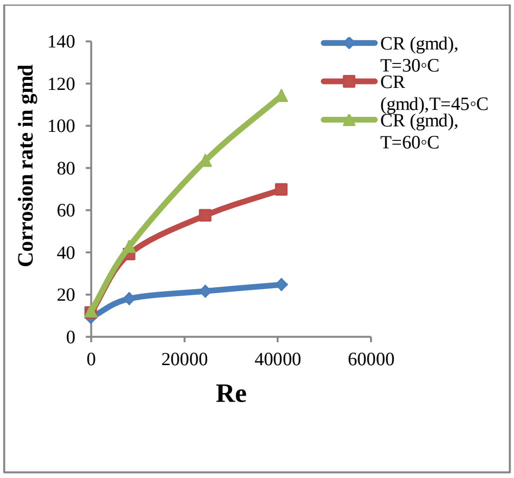

Fig. 2, The relation between corrosion rate and Reynolds no. at different temperatures for 4 h immersion time.

Fig. (2), Shows the variation of corrosion rate of carbon steel in 0.05 N NaCl for three different temperatures (30, 45, and 60^{o}C) with corresponding values of Reynolds number (based on the outer diameter of the specimen) for an immersion period of 4 h and pH of 7.5.

It is clear that from Fig. (2) increasing the flow velocity leads to an increase in the corrosion rate for a given temperature. This can be attributed to the increase in the transport rate of oxygen to the metal surface by eddy transport. The rate of oxygen reduction reaction is generally limited by the rate at which oxygen can reach the surface of the metal. Also, it is clear that corrosion rate increases with increasing temperature at a given velocity. The effect of temperature on corrosion rate for mass transfer controlled systems is dictated by two parameters which affect corrosion rate in conflicting ways that are decreased O_2 solubility and increased O_2 diffusivity. Increasing the temperature will increase the rate of oxygen diffusion to the metal surface by decreasing the viscosity of water and enhancing the corrosion rate.

Fig. (3) Shows the variation of corrosion rate of carbon steel with NaCl concentration of (0.05, 0.03, 0.01, 0.005 N) at 60^{o}C, and 1000 rpm for immersion time of 4 h.

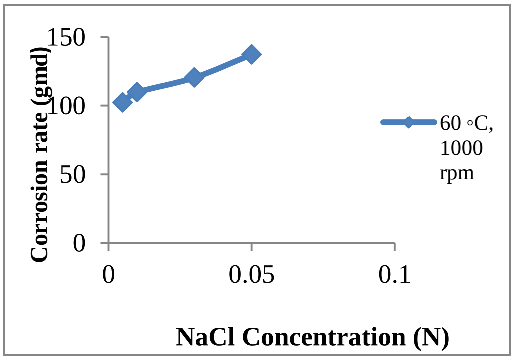

Fig. 3, The relation between corrosion rate and NaCl concentration for immersion time of 4 hr.

It is seen from Fig. (3) that increased concentration of NaCl salts leads to an increased corrosion rate of carbon steel. This is due to an increase in the conductivity of the solution. Chlorides increase the electrical conductivity of water so that the flow of corrosion currents will be facilitated [8, 9].

b. Inhibited solutions

Table (2) displays the low and high levels factor variation interval, the matrix of the central composite rotatable design (CCRD) executed in 0.05 N NaCl (solution d) as given in table (3).

Table (2), Factor variation interval of central composite rotatable design

Factors	Variation levels					Variation intervals
	-1.682	-1	0	1	1.682	ΔX
X_1, Temperature (^{0}C)	30	36	45	54	60	15
X_2, Velocity (rpm)	200	362	600	838	1000	400
X_3, Inhibitors blend concentration (SN+SHMP) (ppm)	600	640	700	760	800	100
	500 + 100	520 + 120	550 + 150	580 + 180	600 + 200	50 50

Table (3), Design matrix of the central composite rotatable design (CCRD)

Number of experiments	Temperature,(°C) X_1	Velocity, (rpm) X_2	Inhibitor blend concentration,(ppm) (SN+SHMP) X_3	Corrosion rates (gmd)
1	1	1	1	1.222
2	1	1	-1	5.653
3	1	-1	1	2.597
4	1	-1	-1	2.903
5	-1	1	1	3.972
6	-1	1	-1	2.292
7	-1	-1	1	3.361
8	-1	-1	-1	1.069
9	-1.68	0	0	1.528
10	1.68	0	0	2.750
11	0	-1.68	0	2.139
12	0	1.68	0	2.445
13	0	0	-1.68	1.833
14	0	0	1.68	0.764
15	0	0	0	3.361
16	0	0	0	3.056
17	0	0	0	3.667
18	0	0	0	4.278
19	0	0	0	3.667
20	0	0	0	3.972

The results of corrosion rate have been analyzed as optimization criterion. The linear model obtained after the eight design points was inadequate. Full fractional experimental (FUFE) design has therefore been upgraded based on a second-order rotatable design. Regression coefficients were determined from experimental data for the following regression equation of corrosion rates by Minitab 16 computer program. Carbon steel corrosion rate is analyzed as function of three variables: temperature, velocity, and inhibitors blend concentrations. All terms regardless of their significance are included in the following equation for 0.05 N NaCl.

$$Y = 3.6319 + 0.2735X_1 + 0.2725X_2 - 0.1876X_3 - 0.0573X_1X_2 - 1.0886X_1X_3 - 0.5921X_2X_3 - 0.3121X_1^2 - 0.2581X_2^2 - 0.6092\,X_3^2 \text{………..} \quad (1)$$

Where Y is the response, that is corrosion rate of carbon steel, and X1, X2, and X3 are the coded values of the test variables, i.e., temperature, rotational velocity, and (SN+SHMP) inhibitors blend's concentration respectively. According to equation (1):

1. The main factors are temperature, and rotational velocity which have positive effects on corrosion rate (i.e., increases corrosion rate). Keeping in mind that temperature is a little more pronounced compared to rotational velocity in affecting carbon steel corrosion rate.
2. The other main factors are (SN+SHMP) inhibitors blend concentration, showed a negative effect (i.e., decreases corrosion rate).

Fig. (4) displays corrosion rate of carbon steel in three different concentrations of NaCl with and without the addition of 600 ppm inhibiting blend (500 ppm SN + 100 ppm SHMP) at 60°C and 1000 rpm for an immersion time of 4 h at pH of 7.5 using weight loss method.

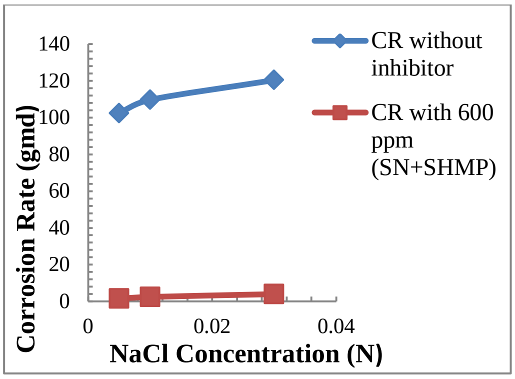

Fig 4, The relation between corrosion rate of carbon steel and NaCl concentration of with and without addition of 600 ppm inhibitors blend for immersion time of 4 h.

Figure (4) shows that the corrosion rate at 60°C and 1000 rpm for the three concentrations (0.005, 0.01, and 0.03 N NaCl) decreases markedly with the addition of inhibitors blend, and this proves the highly inhibitive performance of this blend (SN+SHMP) at higher temperature and velocity (i.e., under dynamic conditions). Table (4) shows the efficiency of the inhibiting blend (600 ppm) in the three different concentrations of NaCl.

Table (4), Efficiencies of the inhibiting blend (600 ppm) in three concentrations of NaCl at 60 °C and 1000 rpm

Concentration (N)	CR (gmd) with inhibitor	CR (gmd) without inhibitor	Efficiency %
0.005	1.5279	102.37	98.5
0.01	2.4446	109.7	97.8
0.03	3.9724	120.4	96.7

2. Corrosion kinetic parameter (Activation energy)

In general, the rate of most chemical reactions increases with temperature following Arrhenius equation [10]. Temperature favors the kinetics of corrosion reactions and more specifically, the anodic dissolution of the metal. The activation energy of the corrosion process can be obtained from the plots of Arrhenius according to the following equation:

$$\text{Corresion rate} = A\, e^{-E_a/RT} \text{……... (2)}$$

Where Ea is the activation energy of the process (J/mol), R is the universal gas constant (8.314 J/(mol.K)), T is the temperature (K) and A is a constant. Taking the logarithm of the Arrhenius equation yields:

$$\text{Log (Corrosion rate)} = \text{Log A} - \frac{E_a}{2.303\ RT} \text{………(3)}$$

The values of activation energy of corrosion in 0.05 N NaCl can be determined from the slope of Log (Corrosion rate) versus 1/T plots.

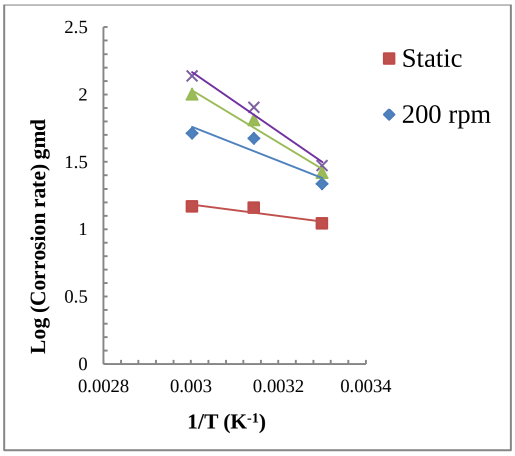

Fig.5, Arrhenius plots of carbon steel in 0.05 N NaCl, uninhibited solution.

Actual values of activation energy for each case of carbon steel corrosion with different temperatures, 30, 45 & 60 ◦C and rotational velocities, i.e., static, 200, 600, and 1000 rpm were plotted according to Eq.3 in Fig. 5. From the gradient of the plotted curves, the calculated Ea values are listed in table (5).

Table (5), Activation energy values at different rotational velocities i.e., Re number.

Velocity (rpm)	Ea (KJ/mol)	Log A
static	8.152	2.462
200	24.37	5.581
600	37.59	7.926
1000	42.99	8.909

The activation energy of an electrochemical process refers to the energy level that must be overcome by one electron in the exchange through the interphase between electrode and electrolyte. Results revealed the activation energy values of the reaction increased with increasing values of rotational velocity. However, rising of temperature acts in the reverse direction due to its duel influence on O_2 dissolved concentration and diffusion coefficient as stated above. Fig.6 presents Arrhenius plots in absence & presence of 700 ppm inhibiting blends for 600 rpm (center condition of rotatable design, i.e., run 9, 10, and 15), which reveal that the activation energy decreases to a value of 16.84 kJ/mol.

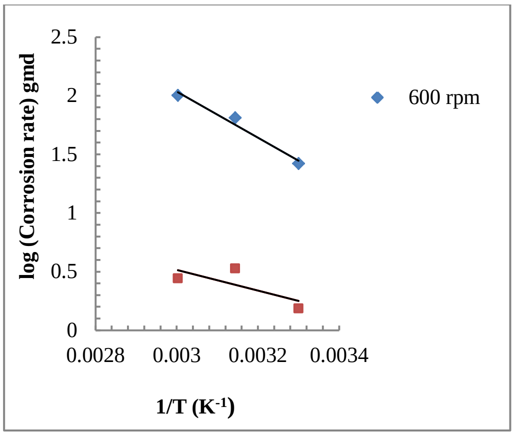

Fig.6, Arrhenius plots for carbon steel corrosion in 0.05 N NaCl, in absence and presence of 700 ppm (550 SN+150 SHMP) inhibitors blend.

3. Polarization Technique

Electrochemical polarization cell was composed of graphite counter electrode, carbon steel specimen as working electrode and saturated calomel (SCE) as a reference electrode.

a. Corrosion Potential

Corrosion potential measurements were carried out for selected conditions of 0.05 N NaCl solutions and also in the other three concentrations (salts concentrations) in absence and presence of corrosion inhibitors blend.

Figs. (7) and (8) show the corrosion potential curves vs. time in 0.05 N NaCl salts solution at three different temperatures (30, 45, and 60 ◦C) and different velocities, i.e., (experiments 9-15) of rotatable design. Fig. (8) presents the results for the three different concentrations (0.005, 0.01, 0.03 N NaCl) in the absence and presence of inhibitors blend for 4 h immersion time.

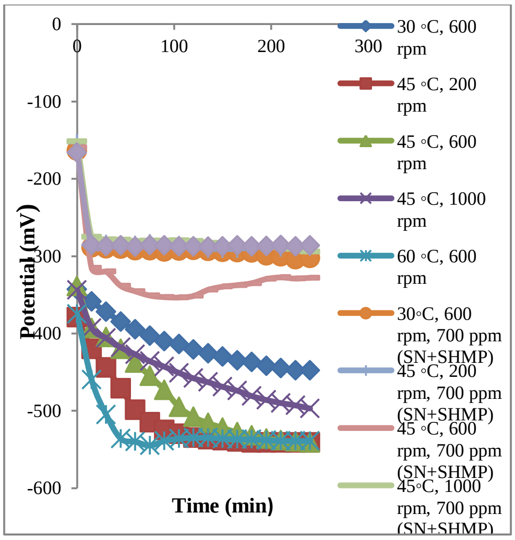

Fig.7, The relation between corrosion potential and time of carbon steel rotating cylinder in 0.05 N NaCl + 0.00736 N Na_2SO_4 at different temperatures and velocities in absence and presence of 700 ppm (550 SN+150 SHMP) for 4 h immersion time, and pH of 7.5.

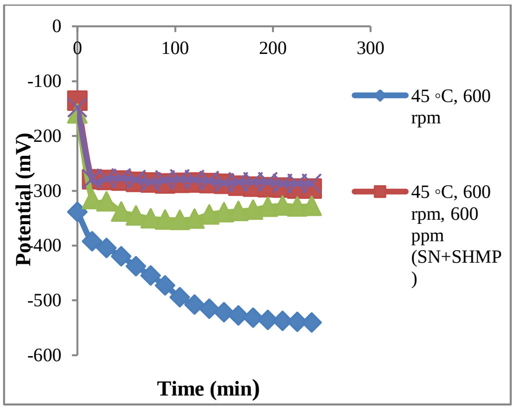

Fig.8. Corrosion potential vs time of carbon steel rotating cylinder in 0.05 N NaCl + 0.00736 N Na_2SO_4 at 45◦C, and 600 rpm with three concentrations of inhibiting blend (600,700, and 800 ppm) for 4 h immersion time at pH of 7.5.

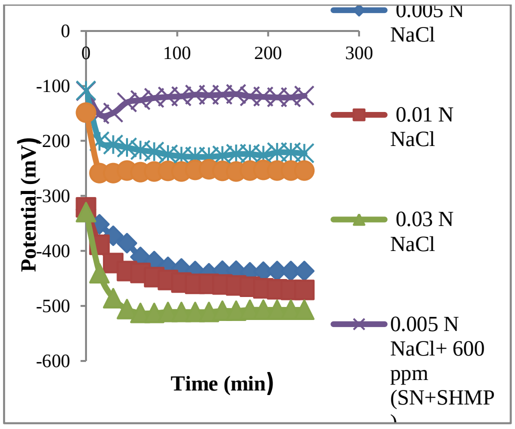

Fig. 9, The relation between Corrosion potential vs time of carbon steel rotating cylinder in three different concentrations of NaCl salts solution at 60^0C, and 1000 rpm, with and without the presence of 600 ppm inhibitors blend for 4 h immersion time, pH = 7.5.

It is clearly seen from Figs. (7) through (9) that the corrosion potential for all salts concentrations of NaCl in absence of inhibitors blend (i.e., SN+SHMP) decreases rapidly with time and finally reaches a steady state value. This variation of corrosion potential with time reveals the corrosivity of water on carbon steel. However, in presence of corrosion inhibitors blend (SN+SHMP), the steady state potential is shifted more towards noble direction by increasing the concentration of inhibiting blend and temperature. Such noble shift of corrosion potential in the range of about 100 to 300 mV would indicate possibly the mechanism of passivation to protect carbon steel in the present aqueous solutions of sodium salts. In addition, a more noble shift illustrates increased anodic polarization for the protection of the metal, i.e., the inhibitors blend is anodically and passively effecting the protection of carbon steel in the present temperature range under dynamic conditions.

b. Electrochemical Polarization Studies

Electrochemical polarization studies were performed for selected points of the rotatable design of 0.05 N NaCl, (experiment 9 to 15).

The polarization behavior of carbon steel in simulated cooling water in presence and absence of inhibitors blend in 0.05 N NaCl are shown in Fig. (10) through (12) respectively, according to the effect of velocity, temperature, and inhibitors blend concentration. Fig. (13) shows the polarization curves for the other three concentrations of NaCl salt (0.005, 0.01, and 0.03 N NaCl):

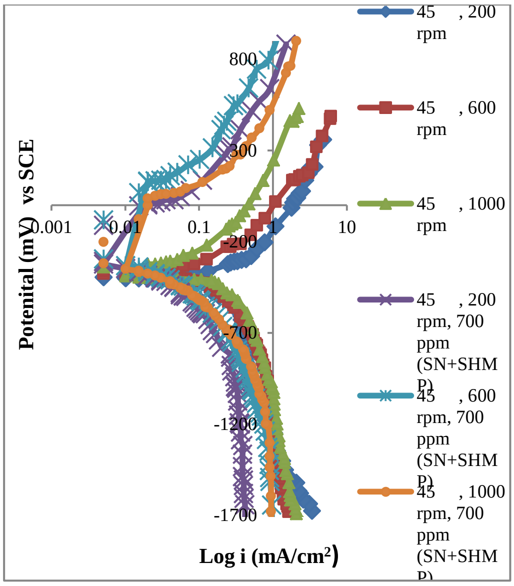

Fig.10, Polarization curves of carbon steel in absence and presence of 700 ppm (550 SN+150 SHMP) inhibitor blend at 45 ◦C and different velocities (run 11, 12 and 15).

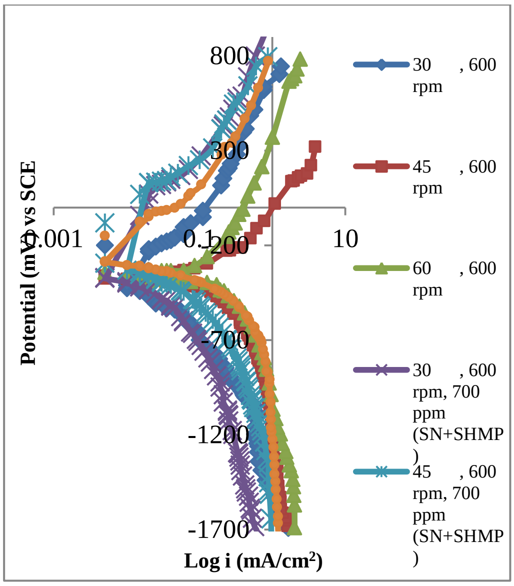

Fig. 11, Polarization curves of carbon steel in absence and presence of 700 ppm (550 SN+150 SHMP) inhibitor blend at 600 rpm and different temperatures (run 9, 10, and 15).

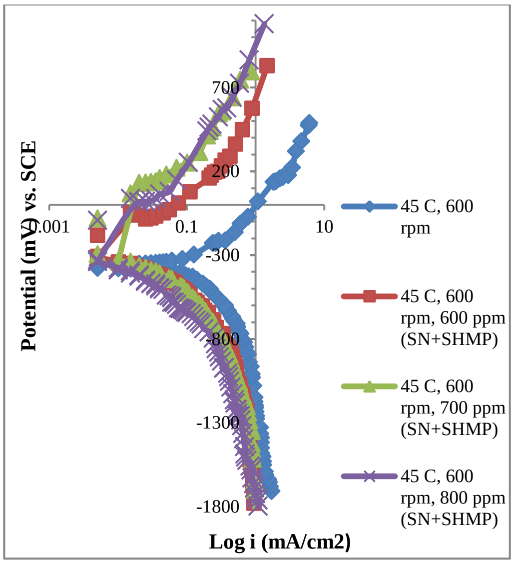

Fig. 12, Polarization curves of carbon steel in absence and presence of different concentrations of inhibitors blends for the central temperature and velocity.

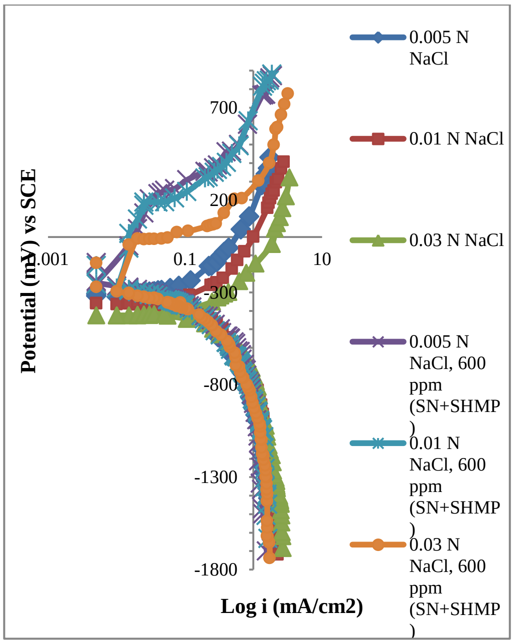

Fig. 13 Polarization curves of carbon steel in different concentrations of NaCl, in absence and presence of 600 ppm (500 SN+100 SHMP) inhibitors blend at 60 ^{0}C and 1000 rpm.

The polarization curves of Fig. (10) and (11) show that the limiting current density is increased with increasing temperature at a constant rpm. Also at a constant bulk temperature the limiting current density increases with increasing rpm in both inhibited and uninhibited solution. The increase in rpm may act to erode any formed layer, increase the metal ion transfer from the metal surface to the solution and the oxygen diffusion from the solution to the metal surface. In contrast, at a constant rpm, the limiting current density is increased with increasing bulk temperature that its effect causes stimulation of the anodic dissolution of iron.

Tables (6) and (7) illustrate the values of corrosion current ($i_{corr.}$), limiting current densities of dissolved oxygen (i_L), and corrosion potentials ($E_{corr.}$) for 0.05 N NaCl solution in absent and presence of the inhibiting blends (run 9 to 15 as selected from the rotatable design). Tables (7) and (8) illustrate the values of ($i_{corr.}$), (i_L) and ($E_{corr.}$) for the others three different concentration of NaCl solutions at 60 ^oC and 1000 rpm (Re of 69031).

Table (6), Values of ($i_{corr.}$), (i_L) and ($E_{corr.}$) for 0.05 N NaCl solution

Run no.	Temp. (^oC)	rpm	Re	i_{corr} (mA/cm^2)	i_L (mA/cm^2)	$E_{corr.}$ (mV)
9	30	600	24499	0.1	0.17	-320
10	60	600	41419	0.3	0.43	-390
11	45	200	10799	0.198	0.29	-394
12	45	1000	53996	0.29	0.4	-340
15	45	600	32398	0.24	0.33	-350

Table (7), Values of ($i_{corr.}$), and ($E_{corr.}$) for 0.05 N NaCl solution with the addition of different concentrations of inhibitors blend according to CCRD

Run no.	Temp. (^oC)	rpm	Re	Inhibitors blend Concentration (SN+SHMP) (ppm)	i_{corr} (mA/cm^2)	$E_{corr.}$ (mV)
9	30	600	24499	700 (550+150)	0.012	-120
10	60	600	41419	700 (550+150)	0.022	-150
11	45	200	10799	700 (550+150)	0.016	-224
12	45	1000	53996	700 (550+150)	0.02	-140
13	45	600	32398	600 (500+100)	0.039	-192
14	45	600	32398	800 (600+200)	0.018	-135
15	45	600	32398	700 (550+150)	0.023	-144

Table (8), Values of ($i_{corr.}$), (i_L) and ($E_{corr.}$) for the different concentrations of NaCl at 60 °C and 1000 rpm (Re = 69031)

NaCl Concentration (N)	$i_{corr.}$ (mA/cm^2)	i_L (mA/cm^2)	$E_{corr.}$ (mV)
0.005	0.29	0.37	-320
0.01	0.36	0.47	-325
0.03	0.45	0.52	-340

Table (9), Values of ($i_{corr.}$), and ($E_{corr.}$) for the different concentrations of NaCl solutions with the addition of 600 ppm (500 SN+100 SHMP) inhibitors blend at 60 °C and 1000 rpm (Re = 69031)

NaCl Concentration (N)	i_{corr} (mA/cm^2)	$E_{corr.}$ (mV)
0.005	0.03	-110
0.01	0.04	-100
0.03	0.05	-130

The formulated inhibitor blend contains sodium nitrite as an anodic inhibitor and sodium hexametaphosphate as a cathodic inhibitor. The corrosion potential values of carbon steel at the various flow rates and temperatures are shifted to more noble direction, due to the fact that $NaNO_2$ is an anodic inhibitor [11]. Furthermore, $(NaPO_3)_6$ acts as cathodic inhibitor [12] is expected to shift the potential strongly towards a negative value. Thus, the net shift of corrosion potential using the present blend is to be in the more noble direction in order to reduce corrosion of carbon steel.

Conclusions

1. Corrosion rate of carbon steel is increased with increasing the temperature range from 30 °C to 60 °C, rotational velocity from 200 to 1000 rpm, and NaCl salts concentration in uninhibited and inhibited solution.
2. Corrosion rate decreases with increases in inhibitors blend concentrations up to 800 ppm for 0.05 N NaCl. While 600 ppm inhibitors blend concentration are very good concentration to give a high efficiency of 98.5%, 97.7%, and 96% for 0.005, 0.01 and 0.03 N NaCl.
3. Corrosion potentials are shifted to the more positive direction with increasing rotational velocity, and inhibitor concentration.
4. The presence of sodium nitrite is very important with sodium hexametaphosphate to protect inhibit carbon steel in the presence of oxygen.
5. The blend of (SN+SHMP) shows excellent efficiencies for almost all concentrations of cooling water systems under a range of flow and temperature conditions.

6. References

References

1. Webster K. SUE, “Effects of NaCl Concentration and Temperature on Corrosion: Understanding Material Interactions in Aqueous Environments”, Boston University

School of Medicine, M.Sc. thesis, 2010.

2. Eddy N.O., Ekwumemgbo P.A., Mamza P.P., "Ethanol extract of terminalia catappa as green inhibitor for the corrosion of mild steel in sulfuric acid", Green chem. Let. Rev. 2(4), 223-231.
3. Farooqi I.H., P.A.Saini, and M. A. Quraishi, "Recent Trends In Cooling Water lnhibitors", Corrosion, 2000.
4. Eswaran M.S., Mathar P.K.,"Physico-chemical evaluation of corrosion inhibitor for carbon steel used in the cooling water system", Corrosion science, vol.38, pp.1783-1790, 1996.
5. Hinton, BRW, Met. Finish, vol.89, pp. 55, 1991.
6. Lake D.L., "Approaching environmental acceptability in cooling water corrosion inhibition, corrosion prevention and control, 1998, p.113.
7. Ivorad Z., R. Lazic´, "Design of Experiments in Chemical Engineering", WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, USA, 2004.
8. Revie R.W. and H.H. Uhlig, "Corrosion and Corrosion Control an Introduction to Corrosion Science and Engineering" fourth edition, John Wiley &Sons, Inc., Hoboken New Jersey, 2008.
9. Shreir L.L., R.A. Jarman and G.T. Burstein, "Corrosion Metal / Environment Reactions" third edition, Butterworth-Heinemann Volume I, Great Britain, 2000.
10. ASTM G1-3, Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.
11. Joseph C.L., Proc.Third Eur. Symp. Inhib., 1970, 19, 791.
12. Rosenfield I.L., " Corrosion Inhibitor " , McGraw Hill , New York , 1981 .
13. Marshall A., "Corrosion Inhibitor for use in natural water system " London , Oyez Scientific and service Ld,1983 .
14. Cohan M., Corrosion Sci. , 1976, 4, 46.